

- (21) Application No 8002208
(22) Date of filing 23 Jan 1980
(30) Priority data
(31) 7901750
(32) 24 Jan 1979
(33) France (FR)
(43) Application published
6 Aug 1980
(51) INT CL³
C08G 77/04
(52) Domestic classification
C3T 6D10 6D11 6D5 6F2
6G10 6G2 6J4 6J5
C3Y B230 B240 B245 B300
F585 H660
(56) Documents cited
None
(58) Field of search
C3T
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(54) Photopolymerisable organopolysiloxane compositions

(57) Organopolysiloxane compositions are prepared by mixing, at a temperature of 5 to 180°C, α,ω -dihydroxydiorganopolysiloxane oils A, silanes B of the formula $Z(G)SiR_aQ_{3-a}$, in which Z represents $CH_2=C(R')-COO$ or HS, G represents an alkylene radical, R and R' represent hydrocarbon radicals, Q represents alkoxy radicals and a has a value ranging from 0 to 2, and catalysts C derived from titanium or tin.

This process is characterised in that the oils A have a viscosity ranging from 70 to 500 mPa.s at 25°C, in that the oils A and the silanes B are mixed in such a way that the molar ratio of hydroxyl radicals in the oils to radicals Q in the silanes ranges from 0.1 to 0.95, and in that the reactants are kept in contact for the time required to remove at most 45% of the theoretical amount of the alcohol QH which should be formed from the radicals OH in the oils A and the radicals Q in the silanes B.

The products obtained by this process can be used, in association with derivatives of benzoin, of xanthone or of thioxanthone, as a starting material for compositions which can be photopolymerised to give non-stick coatings for solids.

SPECIFICATION

Photopolymerisable organopolysiloxane compositions

- 5 The present invention relates to a process for the preparation of liquid organopolysiloxane compositions which are stable on storage, by reacting α , ω -dihydroxydiorganopolysiloxane oils with alkoxysilanes carrying functional radicals which are methacroyloxyalkyl, acroyloxyalkyl or mercaptoalkyl radicals bonded to the silicon atoms. 5
- The invention also relates to organopolysiloxane compositions obtained by mixing either (1) the 10 abovementioned compositions, prepared from α , ω -dihydroxydiorganopolysiloxane oils and alkoxysilanes containing only methacroyloxyalkyl or acroyloxyalkyl radicals (these compositions subsequently being referred to as compositions E₁), with alkoxysilanes containing mercaptoalkyl radicals, or (2) the 10 abovementioned compositions, prepared from α , ω -dihydroxydiorganopolysiloxane oils and alkoxysilanes containing only mercaptoalkyl radicals (these compositions subsequently being referred to as compositions E₂), with alkoxysilanes containing methacroyloxyalkyl or acroyloxyalkyl radicals, or (3) the compositions E₁ 15 with the compositions E₂. The invention also relates to solvent-free compositions E₁, (1), (2) and (3) which can be photopolymerised by ultraviolet irradiation as well as to the use of these photopolymerisable compositions for the non-stick treatment of materials, more especially cellulosic or synthetic materials. 15
- It is known to manufacture liquid organopolysiloxane compositions by reacting hydroxylic organopolysiloxane polymers with alkoxysilanes carrying methacroyloxyalkyl or acroyloxyalkyl radicals bonded to the 20 silicon atoms (see French Patents 1,522,607 and 2,110,115 and U.S. Patent 3,782,940). However, the operating conditions of the processes described in these patents are poorly defined, so that it is rather difficult to be certain of obtaining compositions which can be used without solvents and are stable on storage; very frequently, the resulting compositions gel on storage and/or subsequently lead (after adding 25 photosensitisers) to coatings of which the non-stick properties are not particularly good, despite excessive periods of exposure to radiation, for example periods of more than 50 seconds. 25
- Japanese Kokai 78/118,500 also teaches a process for reacting α , ω -dihydroxypolysiloxanes with trialkoxysilanes containing methacroyloxyalkyl or acroyloxyalkyl radicals, at a high temperature and in the presence of an alcohol having a boiling point which is at least 15°C higher than that of the aliphatic alcohol 30 liberated by the reaction. However, the process is rather long and gives low-viscosity condensates which crosslink rather slowly under the action of UV radiation. 30
- Compositions which have fairly similar structure to those described above, but are prepared by a different process, are described in French Application 2,192,137. This process consists in reacting alkoxysilanes containing methacroyloxyalkyl or acroyloxyalkyl radicals with cyclic or linear organopolysiloxanes, in 35 aprotic solvents and in the presence of basic catalysts. This technique requires the use of solvents and this is always a disadvantage from the industrial point of view; furthermore, it entails a reaction involving rearrangement of the siloxane bonds and this leads to complex mixtures of polymers. 35
- Photopolymerisable compositions which can be used for the non-stick treatment of paper and contain, apart from the photosensitisers, diorganopolysiloxane polymers having ethylenically unsaturated organic 40 radicals, in particular methacroyloxypropyl radicals, are disclosed in U.S. Patent 3,726,710. These methacroyloxypropyl radicals are attached mainly along the chain of the diorganopolysiloxane polymers and not at the end of the chain. To introduce such radicals along the chain, it is necessary to use a more complex technique than that which consists in reacting α , ω -dihydroxydiorganopolysiloxane polymers with 45 alkoxysilanes containing methacroyloxypropyl radicals. Very few details are given of the techniques envisaged; nevertheless substitution reaction is perfectly suitable. 45
- Thus, this process can consist, in a first stage, in manufacturing α , ω -bis-(triorganosiloxy)-diorganopolysiloxane polymers (not readily available on the silicone market) which carry, along the chain, chloroalkyl radicals bonded to the silicon atoms, and then in reacting the chloroalkyl radicals with 50 methacrylic and acrylic acids, in solvents and in the presence of HCl acceptors. A process of this kind requires not only time but also considerable care in order to achieve a high degree of substitution. 50
- It is known to manufacture other types of liquid organopolysiloxane compositions by reacting α , ω -dihydroxydiorganopolysiloxane polymers with alkoxysilanes containing mercaptoalkyl radicals (U.S. Patent 4,066,603). In this process, the reactants are kept in contact in the presence of a basic catalyst, such as potassium hydroxide or a potassium silanolate, and all the alcohol formed is removed during a 55 devolatilisation stage; the use of this type of catalyst involves carrying out a neutralisation stage (in order to prevent the compositions from changing during storage) and sometimes a filtration stage, at the end of the reaction. These steps are restrictive. 55
- Organopolysiloxane compositions which can be photopolymerised after adding photosensitisers and which are formed of organopolysiloxane polymers having alkenyl radicals bonded to the silicon atoms, or 60 optionally organopolysiloxane polymers having SiH bonds, and of silanes or organopolysiloxanes having mercapto-alkyl radicals are described in numerous patents (see French Applications 2,245,729, 2,246,608, 2,257,736 and 2,622,126). These compositions can lead to effective non-stick coatings; however, they still do not possess all the properties which would favour their development in industry. For this they should possess at least the following properties: easy preparation of the various constituents of the compositions, 65 good compatibility of the constituents with one another, low viscosity, and rapid hardening of the 65

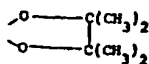
compositions on exposure to ultraviolet radiation.

The present invention is intended to overcome the abovementioned disadvantages. The present invention provides a process for the preparation of organopolysiloxane compositions which are stable on storage, have viscosities ranging from 60 mPa.s to 20,000 mPa.s at 25°C and contain function radicals which are bonded to the silicon atoms, those being methacroyloxyalkyl, acroyloxyalkyl and mercaptoalkyl radicals, in accordance with which process, 1) the following are brought into contact;

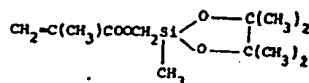
A) α,ω -dihydroxydiorganopolysiloxane;

A) α,ω -dihydroxydiorganopolysiloxane oils in which the organic radicals bonded to the silicon atoms are chosen from methyl, ethyl, n-propyl, vinyl, phenyl and trifluoropropyl radicals, at least 70% of these radicals being methyl radicals and at most 3% being vinyl radicals;

B) silanes of the general formula $Z(G)SiR_a(Q)_{3-a}$ in which the symbol Z represents the radical $CH_2=C(R')$ -COO or the radical HS, the symbols R, which are identical or different, represent methyl, ethyl, n-propyl, vinyl or phenyl radicals, the symbol R' represents a hydrogen atom or a methyl radical, the symbols Q, which are identical or different, represent methoxy, ethoxy or n-propoxy radicals or β -methoxyethoxy radicals, or two symbols Q together represent a radical of the formula



$2)_4\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)(\text{OCH}_3)_2$ and



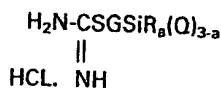
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These silanes can be prepared by reacting intermediates of the formula $\text{Cl-G-SiR}_a(\text{O})_{3-a}$ with organic acids of the formula $\text{CH}_2=\text{C}(\text{R}')\text{COOH}$. The reaction is advantageously carried out in an aprotic solvent, such as N-methylpyrrolidone-2 or N,N-dimethylformamide, and in the presence of a HCl acceptor such as triethylamine. The organic acids can be replaced by their alkali metal salts; in this case, it is unnecessary to introduce a HCl acceptor into the reaction mixture. These silanes can also be purchased on the silicone market.

Concrete examples of silanes of the formula F_2 which may be mentioned are those corresponding to the following formulae: $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{HSCH}_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$, $\text{HS}(\text{CH}_2)_4\text{SiCH}_3(\text{OCH}_3)_2$, $\text{HS}(\text{CH}_2)_4\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5$, $\text{HSCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$, $\text{HS}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$, $\text{HS}(\text{CH}_2)_3\text{SiCH}=\text{CH}_2(\text{OC}_2\text{H}_5)_2$, $\text{HS}(\text{CH}_2)_3\text{SiC}_6\text{H}_5(\text{OCH}_3)_2$ and $\text{HSCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$.

These mercaptosilanes can be prepared by decomposing the isothiuronium salts of the formula:



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with the aid of an alkaline agent such as ammonia (see e.g. U.S. Patent 3,314,982). They can also be purchased on the silicone market.

The catalysts C are chosen from amongst alkyl titanates and poly-(alkyl titanates) and diorganotin salts of aliphatic acids and used at a rate of 0.05 to 2 parts, preferably 0.1 to 1 part, per 100 parts of the mixture of the oils A with the silanes B.

The alkyl titanates usually correspond to the general formula $\text{Ti}[(\text{OCH}_2\text{CH}_2)_b\text{OR}']_4$, in which the symbols R' , which are identical or different, represent alkyl radicals having from 1 to 8 carbon atoms and the symbol b represents zero or 1; when the symbol b represents zero, the alkyl radicals contain from 2 to 8 carbon atoms, such as ethyl, n-octyl, n-propyl, isopropyl, n-butyl, isobutyl, sec.-butyl, n-pentyl, n-hexyl, 2-ethylhexyl or n-heptyl radicals, and when the symbol represents 1, the alkyl radicals are usually methyl or ethyl radicals. Concrete examples of these alkyl titanates which may be mentioned are ethyl, n-propyl, isopropyl, n-butyl, 2-ethylhexyl and β -methoxyethyl titanates.

The poly-(alkyl titanates) can be produced by the partial hydrolysis of the titanates of the formula $\text{Ti}(\text{OR}'')_4$; this formula corresponds to the above formula in which the symbol b represents zero and the symbol R'' represents an alkyl radical having from 2 to 8 carbon atoms.

These polytitanates contain linear structures, each consisting of a series of units of the formula $-\text{TiO}(\text{OR}')_2-$, and/or more complex structures referred to in "The Organic Chemistry of Titanium" R. FELD and P.L. COWE, pages 25 to 31, published by Butterworths, London. The conformation of these polytitanates is closely dependent on the operating conditions of the hydrolysis of the titanates of the formula $\text{Ti}(\text{OR}'')_4$, on the molar ratio of titanates to hydrolysis water and on the nature of the radicals R'' .

These polytitanates should, of course, be stable on storage and soluble in the customary hydrocarbon solvents, such as toluene, xylene and cyclohexane, in a proportion of at least 50 parts per 100 parts of solvents.

The diorganotin salts of aliphatic acids correspond to the formula $(\text{R}'''\text{COO})_2\text{SnT}_2$, in which the symbols R''' , which are identical or different, represent aliphatic hydrocarbon radicals having from 1 to 25 carbon atoms and the symbols T, which are identical or different, represent alkyl radicals having from 1 to 10 carbon atoms.

The aliphatic hydrocarbon radicals represented by the symbols R''' include linear or branched alkyl and alkenyl radicals. Specific alkyl radicals which may be mentioned are methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, 2-ethylhexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-octadecyl, n-eicosyl, n-docosyl and n-pentacosyl radicals. Specific alkenyl radicals which may be mentioned are the radicals corresponding to the formulae: $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2-$, $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_3-$, $\text{CH}_3-\text{CH}=\text{CH}(\text{CH}_2)_5-$, $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_5-$, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8-$, $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}(\text{CH}_2)_8-$ and $\text{CH}_3(\text{CH}_2)_4-(\text{CH}=\text{CH}-\text{CH}_2)_4-(\text{CH}_2)_3-$.

Methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, n-pentyl, n-hexyl, n-octyl and n-decyl radicals may be mentioned as concrete examples of alkyl radicals having from 1 to 10 carbon atoms, which are represented by the symbols T.

The diorganotin salts of aliphatic acids can be pure products or mixtures; the latter can be prepared, for example, by reacting mixtures of carboxylic acids (originating from natural glycerides such as copra oil and palm oil) with diorganotin oxides.

The organotin salts corresponding to the following formulae may be mentioned by way of illustration:

$(\text{CH}_3-\text{COO})_2\text{Sn}(\text{n-C}_4\text{H}_9)_2$, $[\text{CH}_3(\text{CH}_2)_{10}\text{COO}]_2\text{Sn}(\text{n-C}_4\text{H}_9)_2$, $[\text{CH}_3(\text{CH}_2)_{10}\text{COO}]_2\text{Sn}(\text{CH}_3)_2$, $[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO}]_2\text{Sn}(\text{CH}_3)_2$, $[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO}]_2\text{Sn}(\text{n-C}_4\text{H}_9)_2$, $[\text{CH}_3(\text{CH}_2)_{12}\text{COO}]_2\text{Sn}(\text{C}_2\text{H}_5)_2$,

$[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2\text{Sn}(\text{C}_2\text{H}_5)_2$ and $[\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8]_2\text{Sn}(\text{n-C}_4\text{H}_9)_2$.

To carry out the process according to the invention, the first step is to mix the oils A, the silanes B and the catalysts C in the proportions indicated.

Thus, the amounts of the oils A and the silanes B introduced are such that the molar ratio of hydroxyl radicals in the oils A to alkoxy radicals Q in the silanes B ranges from 0.1 to 0.95 and preferably from 0.2 to 0.85. A distribution leading to a molar ratio of less than 0.1 is of no great advantage because it involves the use of large amounts of silanes B; furthermore, a distribution leading to a molar ratio of more than 0.95 causes the formation of organopolysiloxane compositions which are of low stability on storage and/or which exhibit mediocre non-stick properties after hardening.

As already indicated, the catalysts C are introduced at a rate of 0.05 to 2 parts, preferably 0.1 to 1 part, per 100 parts of the oils A and the silanes B taken together.

The mixtures thus formed are treated in the following manner: the three reactants A, B and C are kept in contact at a temperature ranging from 5 to 180°C; during this contact time, at most 45% (for example from 1 to 40%) of the theoretical amount of the alcohol QH which should be formed from the OH radicals in the oils A and the alkoxy radicals Q in the silanes B, present in the mixtures, is removed. The contact time depends on the means used to remove the alcohol and also on the heating conditions. It is at least 5 minutes and preferably at least 15 minutes and can exceed several days. By operating at atmospheric pressure and at temperatures exceeding 100°C, for example at 120 to 160°C, whilst at the same time allowing at most the abovementioned percentage of the alcohol QH to leave the reaction mixture during heating, the contact times do not generally exceed 90 minutes. By facilitating the removal of the alcohol QH with the aid of a stream of inert gas which passes through the reaction mixture, or by using a pressure below atmospheric pressure, these contact times can be further reduced and can become less than, for example, 60 minutes.

It is not recommended to exceed 180°C for fear of obtaining high-viscosity compositions which are unstable on storage.

When operating at much lower temperatures, namely of the order of 20 to 50°C, the reactants must be left in contact for at least 48 hours; the requisite amount of alcohol QH is then removed, preferably at the end of contact period, by heating gently under a pressure below atmospheric pressure or solely under the action of a pressure below atmospheric pressure.

If more than 45% of the theoretical amount of the alcohol QH which should be formed is removed during these processes, the resulting compositions are likely to gel during storage.

In accordance with a variant of the process described above, the three reactants are kept in contact for at least 10 hours, at a temperature ranging from 5°C to 90°C, and none of the alcohol QH is removed during this time. This method of treatment is very simple but it requires fairly long periods of time which are longer, the lower is the temperature. At about 5 to 20°C, the reactants must be left in contact for at least 72 hours, but at about 70-90°C; generally no more than about ten hours are required.

The choice of the method of treatment will depend on the manufacturing requirements (the residence time, the heating means and the manner in which the reactors are fitted out) and on the nature of the alcohol QH. The removal of a volatile alcohol QH, such as methanol or ethanol, by heating the reaction mixture, will require less heat than the removal of butanol or even hexanol.

The compositions obtained in accordance with this process have a viscosity ranging from 60 mPa.s to 20,000 mPa.s at 25°C and more frequently from 150 mPa.s to 15,000 mPa.s at 25°C.

They are stable on storage in closed opaque containers. However, the viscosity of some of these compositions can change during the first few weeks after they have been manufactured, during which period it increases, for example, from, say, 300 mPa.s at 25°C to 1,000 mPa.s at 25°C, but it subsequently stabilises and does not change further.

By virtue of the process for their preparation, these compositions contain, bonded to the silicon atoms, either methacroyloxyalkyl and/or acroyloxyalkyl functional radicals provided by the silanes of the formula F_1 , or mercaptoalkyl radicals provided by the silanes of the formula F_2 .

As mentioned initially, the compositions containing methacroyloxyalkyl and/or acroyloxyalkyl radicals are referred to as compositions E_1 and those containing mercaptoalkyl radicals are referred to as compositions E_2 .

Apart from the preparative process which has now been described, the present invention provides liquid compositions which are characterised in that they are obtained:

either by mixing the compositions E_1 with the silanes of the formula F_2 , the representative amounts of the compositions E_1 and the silanes F_2 present being such that the molar ratio of the radicals of the formula $\text{CH}_2=\text{C}(\text{R}')\text{COO}-$, provided by the compositions E_1 , to the radicals of the formula $\text{HS}-$, provided by the silanes F_2 , is at least 0.05 and in practice ranges from 0.05 to 15 and preferably from 0.2 to 12; these compositions are referred to as H_1 ,

or by mixing the compositions E_2 with the silanes of the formula F_1 , the respective amounts of the compositions E_2 and the silanes F_1 present being such that the molar ratio of the radicals of the formula $\text{CH}_2=\text{C}(\text{R}')\text{COO}-$, provided by the silanes F_1 , to the radicals of the formula $\text{HS}-$, provided by the compositions E_2 , is at least 0.05 and in practice ranges from 0.05 to 15 and preferably from 0.1 to 8; these compositions are referred to as H_2 ,

or by mixing the compositions E_1 with the compositions E_2 , the respective amounts of the compositions E_1 and E_2 present being such that the molar ratio of the radicals of the formula $\text{CH}_2=\text{C}(\text{R}')\text{COO}-$, provided by the

compositions E_1 , to the radicals $HS\cdot$, provided by the compositions E_2 , is at least 0.5 and in practice ranges from 0.05 to 15 and preferably from 0.1 to 10; these compositions are referred to as H_3 .

These liquid compositions have viscosities ranging from 60 mPa.s at 25°C to 20,000 mPa.s at 25°C and generally from 100 mPa.s to 15,000 mPa.s at 25°C. When the molar ratio $CH_2=C(R')COO/SH$ ranges from 0.05 to 15, these compositions are sensitive to radiation and should preferably be manufactured at the time of use; however, they are stable on storage in closed opaque containers for about 48 hours.

Each composition H_1 , H_2 and H_3 can be prepared by simply mixing the appropriate constituents at ambient temperature and at atmospheric pressure. This process does not therefore require particular precautions; nevertheless, if one or both of the constituents contain alkoxy radicals Q which are very sensitive to hydrolysis (such as methoxy radicals), and if the atmosphere is also very moist, it is desirable to carry out the mixing under a dry atmosphere, but this is not necessary in the majority of cases.

Within the limit of their mutual compatibility, the constituents of the compositions H_1 , H_2 and H_3 can be mixed in any proportions; however, of the resulting compositions, those in which the molar ratios of the radicals of the formula $CH_2=C(R')COO$ to the radicals of the formula HS are below 0.05 are of little value for the non-stick treatment of a variety of different materials.

In fact, the compositions H_1 , H_2 and H_3 , after photosensitisers have been added, are mainly intended to be deposited in thin layers onto cellulosic or synthetic flat supports; these layers are then hardened by exposure to radiation and more especially to ultraviolet radiation. Coatings are therefore sought which have good non-stick properties with respect to sticky, glutinous, viscous or moist substances.

Apart from the compositions H_1 , H_2 and H_3 , the compositions E_1 , but not the compositions E_2 , can also be used for non-stick treatment; the compositions E_2 , after the addition of photosensitisers and hardening by exposure to radiation, do not always make it possible to obtain non-stick coatings having good resistance to gumming.

The present invention therefore also provides compositions which can be photopolymerised by exposure to ultraviolet radiation and which are characterised in that they contain 100 parts (by weight) of the composition E_1 , H_1 , H_2 or H_3 and 0.1 to 10 parts, preferably 0.2 to 8 parts, of photosensitisers (or photoinitiators).

These photopolymerisable compositions can be obtained simply by mixing the composition E_1 , H_1 , H_2 or H_3 with the photosensitiser, at ambient temperature and atmospheric pressure. The time for which the compositions are mixed with the photosensitisers depends on the amounts of photosensitisers introduced and on their solubility in the compositions. Generally, a period of 30 minutes to 3 hours is required.

The photosensitisers are preferably chosen from derivatives of benzoin, of xanthone and of thioxanthone.

Concrete examples of such photosensitisers which may be mentioned are alkyl ethers of benzoin (in which the alkyl radical contains from 1 to 6 carbon atoms), such as the n-propyl, isopropyl, n-butyl and isobutyl ethers, or mixtures thereof, 3-chloroxanthone, 3-methoxyxanthone and 2-chlorothioxanthone.

Other types of photosensitisers can also be employed, such as aromatic ketone derivatives, for example acetophenone, benzophenone and 4,4'-bis-(dimethylamino)-benzophenone. However, these last compounds sometimes give poorer results than the preceding compounds, and a co-initiator, for example triethylamine or triethyl phosphite, should be added.

The photopolymerisable compositions are used more especially, as already indicated, for the non-stick treatment of sheets of cellulosic or synthetic materials. For this purpose, they are generally deposited onto these surfaces at a rate of 0.5 to 5 g/m² with the aid of devices employed on industrial machines, for example several rollers placed one above the other, the bottom roller being in contact with the compositions to be deposited and the top roller being in contact with the surfaces to be treated (see e.g. French Application 2,207,811).

The photopolymerisable compositions (deposited in this way in the form of thin layers) are hardened by exposure to ultraviolet radiation produced by, for example, xenon or mercury arc lamps, the emission spectrum of which ranges from 250 to 450 nm. The exposure time is very short; it is generally less than 30 seconds and preferably less than 20 seconds and can be as short as, say, 1 second. The exposure time is particularly short in the case of the compositions- H_1 , H_2 and H_3 in which the molar ratio of radicals $CH_2=C(R')COO/SH$ ranges from 0.05 to 15. In other words, the presence of SH radicals contributes to a reduction of this exposure time.

However, the photopolymerisable compositions of the invention can generally be applied to all materials which are in contact, or are to be in contact, with sticky, viscous or pasty substances or substances which release moisture. The nature and origin of these materials are varied. Such surfaces include the various types of paper (such as Kraft paper for which the degree of beating is of no consequence, glassine and parchment), cardboard, imitation parchment, paper coated with polyethylene or with carboxymethylcellulose, sheets of regenerated cellulose or of cellulose acetate, plastic sheets, such as polyethylene, polypropylene and polyethylene terephthalate sheets, metal sheets, fabrics based on synthetic fibres, glass fibres or asbestos fibres, and non-woven fibrous materials, whether these be based on cellulosic fibres or synthetic fibres or a mixture of these fibres.

The materials rendered non-stick in this way can be used as spacers, separating supports, paper and films for transfers, and packaging for 1. sticky materials, such as confectionery, pastries, crude rubber, pitch and bitument, and wax, or for 2. foodstuffs which release moisture, such as fish, meat and cheese.

The following Examples further illustrate the invention.

The parts and percentages are expressed by weight.

Example 1

a) 95.4 parts of an α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of approximately 100 mPa.s at 25°C and containing 0.7% of hydroxyl groups, 4.6 parts of the silane of the formula: $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, and 0.2 part of tetraisopropyl titanate are introduced into a reactor equipped with a stirrer, a thermometer sleeve and a swan neck surmounted by an analyser.

The molar ratio of OH radicals in the oil to OCH_3 radicals in the silane is about 0.7.

The contents of the reactor are heated gradually from 23°C to 150°C over a period of 28 minutes; during this heating, 0.19 part of methanol is collected in a collector downstream of the analyser. Given that the expected theoretical amount of methanol is 1.26 parts, the percentage extracted represents about 15% of this amount. The limpid liquid obtained has a viscosity of 1,000 mPa.s at 25°C.

b) 4 parts of a photoinitiator consisting of a mixture of the butyl ether and isobutyl ether of benzoin (in practice distributed in the weight ratio 50/50) are added to 100 parts of the liquid prepared above, and the whole is stirred at ambient temperature for 2 hours.

The resulting mixture is then deposited, at a rate of 2 g/m², onto a Kraft paper (prepared from a bleached pulp beaten to 64° on the Shopper scale) which weighs 67 g/m² and has been surfaced with cellulosic polymers and supercalendered.

Deposition is carried out with the aid of a coating system which mainly comprises 3 rollers arranged one above the other. The bottom cylinder is immersed in a tank filled with the mixture to be deposited onto the paper, and impregnates the transfer roller located above it with this mixture; this transfer roller in turn impregnates a coating roller which is kept in continuous contact with the sheet of paper.

The layer of silicone applied to the paper is hardened by exposure to ultraviolet radiation for 10 seconds. This radiation is emitted by a lamp, without reflector, containing mercury vapour and the vapour of metal iodides, the frontal zone of which lamp is located at a distance of 1 cm from the surface of the paper; the emission spectrum ranges from 275 to 450 nm with a maximum at between 360 and 380 nm. The power received by the sample is of the order of 9.4 to 9.8 W/cm².

By rubbing the finger over the coated face of the paper, it is found that there are no signs of gumming; the layer is thus suitably hardened and it does not migrate.

Furthermore, test-pieces are manufactured by initially cutting samples of dimensions 200 × 50 mm from the silicone-coated paper. An adhesive tape of dimensions 150 × 19 mm is then applied to the coated face of each sample.

The test-pieces are placed on a metal plate and then left for 20 hours at 70°C; during this period, they are subjected to a pressure of 18 g/cm² by placing small steel plates over their entire surface.

After this treatment, the test-pieces are exposed to the atmosphere for 1 hour, the temperature being about 20°C. The adhesive tape on each test-piece is then detached from the surface of the paper by pulling with the aid of a tensile strength tester, the speed of detachment being 200 mm/minute. A detachment force of 12 g per 1 cm width of the tape is recorded. This value demonstrates the good non-stick properties provided by the silicone coating.

Example 2

8 experiments are carried out by following the procedure described in part (a) of Example 1; however, the respective amounts of the α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of 100 mPa.s at 25°C, and of the silane of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, and also the method of heating the 3 reactants, are varied. 0.2 part of tetraisopropyl titanate is still incorporated for each experiment.

The data relating to the manner in which these experiments are carried out, and to the viscosity of the compositions formed, are shown in Table I below:

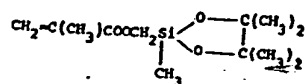
TABLE I

Experiment	Oil Amount in parts	Silane Amount in parts	Molar ratio OH/OCH ₃	Method of heating	Amount of methanol extracted in %, relative to the theoretical amount	Viscosity, in mPa.s at 25°C, of the composition obtained	
						On leaving the reactor	After conditioning for 30 days in a closed opaque container
d ₁	97.9	2.1	1.5	from 23 to 160°C in 40 minutes	10	330	gelled
d ₂	96.6	3.4	0.95	from 23 to 160°C in 25 minutes	19	600	2,500
d ₃	95.4	4.6	0.7	at 23°C for 96 hours	zero	350	1,000
d ₄	95.4	4.6	0.7	from 23 to 90°C in 30 minutes + 1 hour at 90°C	1.9	360	1,000
d ₅	95.4	4.6	0.7	from 23 to 160°C in 60 minutes	50	2,400	gelled
d ₆	93.8	6.2	0.5	from 23 to 140°C in 30 minutes	15	450	2,000
d ₇	90.1	9.9	0.3	from 23 to 140°C in 30 minutes	11	200	240
d ₈	75.1	24.9	0.1	from 23 to 150°C in 40 minutes	15	240	300

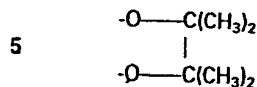
The non-stick properties provided by the deposition and subsequent hardening of these various compositions on paper is measured in accordance with the procedure in part b of Example 1. It is found that all the compositions provide good durable non-stick properties (no gumming with the finger and a detachment force of less than 20 g/cm), with the exception of the compositions of experiments d₁ and d₅. These two compositions are not stable on storage and they also harden unsatisfactorily on exposure to ultraviolet radiation; in fact, they require an exposure time of 90 seconds, instead of the 25 to 10 seconds required in the case of the other compositions, whilst at the same time producing mediocre results in terms of the non-stick properties (gumming with the finger).

Example 3

93 parts of an α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of approximately 100 mPa.s at 25°C and containing 0.7% of hydroxyl groups, 7 parts of a silane of the formula

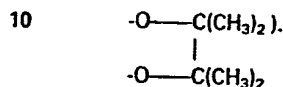


and 0.2 part of isopropyl titanate are introduced into the reactor used in Example 1. The molar ratio of OH radicals in the oil to radicals



5

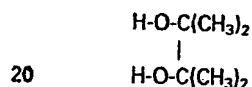
in the silane is about 0.7 (2 SiOH radicals are counted per radical



10

The contents of the reactor are heated from 23°C to 140°C over a period of 35 minutes; they are then kept at this temperature for 30 minutes.

During this treatment, some traces of water are collected, but no traces of the diol of the formula



15

20

are collected. The resulting limpid liquid has a viscosity of 315 mPa.s at 25°C.

The procedure in part b of Example 1 is then followed and the Kraft paper, weighing 67 g/m², is thus treated with a mixture comprising 100 parts of the above liquid and 4 parts of the abovementioned mixture of the butyl ether and isobutyl ether of benzoïn. It is found that the silicone layer, hardened by exposure to ultraviolet radiation for 20 seconds, resists gumming, and that the force required to detach the adhesive tape from the paper is of the order of 15 g/cm.

25

Example 4

30 3 experiments are carried out by following the procedure described in part (a) of Example 1; however, the α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of 100 mPa.s at 25°C is replaced by any one of the 3 α,ω -dihydroxydimethylpolysiloxane oils A₁, A₂ and A₃, which have the following characteristics:

30

A₁: viscosity of 60 mPa.s at 25°C and proportion of OH groups of 3.7%

35 A₂: viscosity of 500 mPa.s at 25°C and proportion of OH groups of 0.40%

A₃: viscosity of 750 mPa.s at 25°C and proportion of OH groups of 0.3%.

35

The data relating to the method by which these experiments are carried out, in particular the respective amounts of the oils A₁, A₂ and A₃ and of the silane of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, and also the viscosity of the compositions formed, are shown in Table II below.

40 For each experiment, isopropyl titanate is used at a dose of 0.2 part per 100 parts of the oil and silane taken together; furthermore, the molar ratio of SiOH radicals in each oil to OCH₃ radicals in the silane remains constant (of the order of 0.7).

40

TABLE II

Experiment	Nature of the oil and amount used	Amount of silane	Method of heating	Amount of methanol extracted in %, relative to theory	Viscosity, in mPa.s at 25°C, of the compositions obtained	
					on leaving the reactor	after 30 days in a closed opaque container
e ₁	(A ₁) 79.3	20.7	from 23°C to 160°C in 40 minutes	26	50	250
e ₂	(A ₂) 95.4	4.60	from 23°C to 145°C in 49 minutes	4.8	5,000	10,000
e ₃	(A ₃) 98.06	1.94	from 23°C to 145°C in 49 minutes	traces	35,000	gelling

The non-stick properties provided by the deposition and subsequent hardening of the compositions of experiments e_1 , e_2 and e_3 on paper is measured in accordance with the procedure in part (b) of Example 1. It is found that:

- the use of the oil A_1 , in experiment e_1 , leads to mediocre non-stick properties since the detachment force is 80 g/cm, and also crosslinking requires a fairly long exposure time (45 seconds).
the use of the oil A_2 , in experiment e_2 , leads to good non-stick properties, the detachment force being 30 g/cm for a cross linking time for 20 seconds, and
the use of the oil A_3 , in experiment e_3 , leads to poor non-stick properties, even though the crosslinking time is 55 seconds; the coating is easily removed by gumming and the composition also gels rapidly on storage.

Example 5

The composition having a viscosity of 350 mPa.s at 25°C (shown under experiment number d_3 in Table I of Example 2), which is prepared by stirring the α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of 100 mPa.s at 25°C with the silane of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, at ambient temperature for 96 hours, in the presence of isopropyl titanate, is used.

Varying amounts of the mercaptosilane of the formula $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ are associated with this composition, subsequently referred to as P_1 , so as to obtain a different molar ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}$ to HS radicals for each new composition formed. Varying amounts of the photoinitiator used in part (b) of Example 1 are also added. The time of exposure to ultraviolet radiation which makes it possible to achieve effective and durable non-stick properties (no gumming and a detachment force of less than 30 g/cm) is then determined in accordance with the technique also taught in part (b) of Example 1.

The data relating to the proportion of the constituents in the new compositions, and also the photo-crosslinking times, are recorded in Table III below:

TABLE III

Experiment	Constitution of each new composition			Molar ratio $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO/HS}$	Amount of the photo-initiator	Time of exposure to ultra-violet radiation in seconds
	Amount of the composition F_1	Amount of the mercapto-silane				
f_1	100	0				
$\text{f}_{1'}$	100	0		4	10	
f_2	99.6	0.4	9	1	20	
$\text{f}_{2'}$	99.6	0.4	9	4	4	
f_3	98.8	1.2	3	1	20	
$\text{f}_{3'}$	98.8	1.2	3	4	2	
f_4	96.3	3.7	1	1	10	
$\text{f}_{4'}$	96.3	3.7	1	4	2	
f_5	88.7	11.3	0.3	1	8	
$\text{f}_{5'}$	88.7	11.3	0.3	4	2	
				1	2	

It is apparent from these results that the introduction of the mercaptosilane has a beneficial effect; thus, it makes it possible, on the one hand, substantially to reduce the times of exposure to radiation, and, on the other hand, to choose small amounts of the photoinitiator.

5 *Example 6*

(a) 96.3 parts of an α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of approximately 100 mPa.s at 25°C and containing 0.7% of hydroxyl groups, 3.7 parts of a silane of the formula $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ and 0.2 part of isopropyl titanate are introduced into the reactor used in Example 1.

The molar ratio of OH radicals in the oil to OCH_3 radicals in the mercaptosilane is about 0.7.

10 The contents of the reactor are stirred for 96 hours at ambient temperature. This results in the formation of a composition, subsequently referred to as P_2 , which is limpid and has a viscosity of 300 mPa.s at 25°C; this viscosity reaches 1,000 mPa.s at 25°C after conditioning for 30 days in a closed container; it then stabilises at this value.

Varying amounts of the methacryloxysilane of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ are associated with this composition P_2 so as to give a different ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-$ to HS radicals for each new composition formed. Varying amounts of the photoinitiator used in part (b) of Example 1 are also added. The exposure time which makes it possible to achieve effective and durable non-stick properties, characterised by a good resistance to gumming and a detachment force of less than 30 g/cm, is then measured.

20 The data relating to the constitution of the new compositions, and also the photocrosslinking times, are summarised in Table IV below:

TABLE IV

Experiment	Constitution of each new composition			Molar ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO-}$ to HS radicals	Amount of the photo-initiator	Time of exposure to ultra-violet radiation in seconds
	Amount of the composition P_2	Amount of the methacryloyloxysilane				
g	100	0			0	10
g'	100	0			4	10
g ₁	98.6	1.4	0.3		4	5
g ₁ '	98.6	1.4	0.3		1	6
g ₂	95.5	4.5	1		4	1
g ₂ '	95.5	4.5	1		4	7
g ₃	87.6	12.4	3		4	6
g ₃ '	87.6	12.4	3		1	7
g ₄	70.2	29.8	9		4	6
g ₄ '	70.2	29.8	9		1	12

The coatings obtained from the compositions of experiments g and g' can fairly easily be removed by rubbing with the finger, even though the force required to detach the adhesive tape placed on their surface is less than 30 g/cm.

It is apparent from this table that the presence of methacroyloxysilane is necessary in order to have a good resistance to gumming; it also makes it possible to reduce the photocrosslinking time; the best results are achieved with the compositions of experiments g₂ and g₂', these compositions possessing a molar ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}$ to HS radicals of the order of 1.

(bi) By way of comparison, the procedure described in paragraph (ai) above is repeated, except that 97.4 parts of the α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of 100 mPa.s at 25°C and 2.6 parts of the silane of the formula $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ are employed. These amounts define a molar ratio of OH radicals in the oil to OCH_3 radicals in the mercaptosilane of about 1.

The resulting composition has a viscosity of 425 mPa.s at 25°C.

24.7 parts of the abovementioned methacroyloxysilane are associated with 75.3 parts of this composition, thus establishing a molar ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}$ - to HS- radicals of the order of 1.

4 parts of the photoinitiator used in part (b) of Example 1 are added to 200 parts of this mixture and the whole is subjected to ultraviolet radiation. For an exposure time of 20 seconds, it is found that the hardened silicone layer does not resist gumming with the finger; consequently, in view of the results shown in Table IV, it is necessary to employ (before adding the methacroyloxysilane) a starting composition having a molar ratio of OH radicals in the oil to OCH_3 radicals in the mercaptosilane of less than 1.

Again by way of comparison, the procedure described above in (ai) is repeated, except that 98.4 parts of an α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of 750 mPa.s at 25°C and containing 0.3% of OH groups are used in place of the oil having a viscosity of 100 mPa.s at 25°C and 1.6 parts of the silane of the formula $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ are used, the molar ratio of OH radicals in the oil to OCH_3 radicals in the mercaptosilane still being 0.7.

It is found that the liquid formed, which has a viscosity of 30,000 mPa.s at 25°C, is not stable on storage; in particular, it gels after conditioning for about ten days in a closed container at ambient temperature. Consequently, in view of the stability exhibited by the composition P₂, it is necessary to use an oil having a viscosity of less than 750 mPa.s.

Example 7

Several compositions are manufactured by simply mixing, at ambient temperature, varying amounts of the composition P₁ (described in Example 5), prepared from the α,ω -dihydroxydimethylpolysiloxane oil having a viscosity of 100 mPa.s at 25°C and from the methacroyloxysilane of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, with the composition P₂ (described in Example 6), prepared from the same α,ω -dihydroxydimethylpolysiloxane oil and from the mercaptosilane of the formula $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$.

The effectiveness of each composition, from the point of view of the non-stick properties, is determined in accordance with the procedure indicated in part (b) of Example 1; two different amounts of the photoinitiator formed by mixing the butyl ether and isobutyl ether of benzoin in a weight ratio of 50/50 are incorporated into each composition, and each new mixture is subjected to ultraviolet radiation emitted by the equipment described in part (b) of Example 1. The exposure times which make it possible to obtain good non-stick properties which are retained with time (on the one hand the resistance of the coating to gumming with the finger, and on the other hand a force required to detach the adhesive tape of less than 30 g/cm) are then measured.

The data relating to the constitution of the compositions and to the crosslinking times are summarised in Table V below:

TABLE V

Experiment	Constitution of each new composition			Molar ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}$ to HS radicals	Amount of the photo-initiator	Photo-crosslinking time
	Amount of the composition F_1	Amount of the composition P_2				
K	100	0			4	8
K'	0	100			0	10
K ₁	22.5	77.5	0.3		4	1
K _{1'}	22.5	77.5	0.3		1	4
K ₂	49.1	50.9	1		4	1
K _{2'}	49.1	50.9	1		1	2
K ₃	74.3	25.7	3		4	3
K _{3'}	74.3	25.7	3		1	6
K ₄	89.7	10.3	9		4	12
K _{4'}	89.7	10.3	9		1	24

It should be noted that, in the case of experiment K', the deposited layer does not resist gumming with the finger.

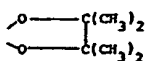
It is apparent from the results shown in the table that the mixed compositions in which the molar ratio of radicals $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}$ to HS radicals ranges from 0.3 to 3 are crosslinked in very short times with a small amount of photoinitiator.

CLAIMS

1. Process for the preparation of an organopolysiloxane composition having a viscosity from 60 mPa.s to 20,000 mPa.s at 25°C and contains methacroyloxyalkyl, acroyloxyalkyl or mercaptoalkyl radicals bonded to the silicon atoms, which process comprises contacting the following:

A) an α,ω -dihydroxydimethylpolysiloxane oil in which the organic radicals bonded to the silicon atoms are methyl, ethyl, n-propyl, vinyl, phenyl or trifluoro-propyl radicals at least 70% of these radicals being methyl radicals and at most 3% being vinyl radicals, the oils having a viscosity from 70 to 500 mPa.s at 25°C;

B) a silane of the general formula $\text{Z}(\text{G})\text{SiR}_a(\text{Q})_{3-a}$ in which Z represents the radical $\text{CH}_2=\text{C}(\text{R}')\text{-COO}$ or HS, in which each R, which is identical or different, represents a methyl, ethyl, n-propyl, vinyl or phenyl radical, R' represents a hydrogen atom or a methyl radical, each Q, which is identical or different, represents a methoxy, ethoxy, n-propoxy or β -methoxyethoxy radical, or two symbols Q together represent a radical, of the formula



G represents a linear or branched alkylene radical having from 1 to 8 carbon atoms and represents a value from 0 to 2, the molar ratio of hydroxyl radicals in A to radicals Q in B being from 0.1 to 0.95; and

C) a catalyst which is an alkyl titanate or poly (alkyl titanate) or a diorganotin salt of an aliphatic acid, in an amount of 0.05 to 2 parts per 100 parts of the mixture of A and B; and 2) allowing A, B and C to interact at a temperature from 5°C to 180°C for the time required to remove at most 45% of the theoretical amount of the alcohol QH which should be formed from the radicals OH in the oil A and the radicals Q in the silane B.

2. Process according to claim 1 in which the mole ratio of hydroxyl radicals in A to radicals Q in B is 0.2 to 0.85.

3. A modification of a process according to Claim 1 or 2, in which there is substantially no removal of the alcohol QH and the reactants A, B and C are simply kept in contact for at least 10 hours, at a temperature from 5°C to 90°C.

4. Process according to claim 1 substantially as described in any one of the Examples.

5. An organosiloxane composition whenever prepared by a process as claimed in any one of claims 1 to 4.

6. A composition having a viscosity from 60 mPa.s to 20,000 mPa.s at 25°C and containing a mixture of radicals $\text{CH}_2=\text{C}(\text{R}')\text{COO-}$ and HS- in a numerical ratio of these radicals of more than 0.05:1 the composition being either a mixture of a composition as claimed in Claim 5, in which Z represents the radical $\text{CH}_2=\text{C}(\text{R}')\text{COO}$, with a silane $\text{HS}(\text{G})\text{SiR}_a(\text{Q})_{3-a}$, or a mixture of a composition as claimed in Claim 5 in which Z represents the radical HS, with a silane $\text{CH}_2=\text{C}(\text{R}')\text{COO}(\text{G})\text{SiR}_a(\text{Q})_{3-a}$, or a mixture of a composition as claimed in Claim 5, in which Z represents the radical $\text{CH}_2=\text{C}(\text{R}')\text{COO}(\text{G})\text{SiR}_a(\text{Q})_{3-a}$, with a composition as claimed in Claim 5, in which Z represents the radical HS, the respective amounts of the mixture being chosen so as to give a numerical ratio of radicals $\text{CH}_2=\text{C}(\text{R}')\text{COO}$ to HS radicals of more than 0.05:1

7. A composition which can be photo-polymerised by ultraviolet irradiation and which comprises 0.1 to 10 parts of a photosensitiser which is a derivative of benzoin, of xanthone or a thioxanthone, per 100 parts by weight of either a composition as claimed in Claim 5, in which the symbol Z represents the radical $\text{CH}_2=\text{C}(\text{R}')\text{COO}$ or a composition as claimed in claim 6.

8. Process for providing a substrate with a non-stick coating which comprises coating the substrate with a composition as claimed in Claim 6 and subjecting the coating to ultraviolet light.

9. A substrate whenever provided with a non-stick coating by a process as claimed in claim 8.